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Branch, Byron, Gray, Ibbotson, and Worrall.

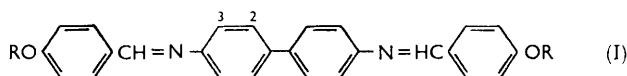
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622. Mesomorphism and Chemical Constitution. Part XII.¹ The Preparation and Mesomorphic Properties of Substituted 4,4'-Di-(*p*-*n*-alkoxybenzylideneamino)biphenyls.

By S. J. BRANCH, D. J. BYRON, G. W. GRAY, A. IBBOTSON, and B. M. WORRALL.

The melting points and mesomorphic transition temperatures of certain (alkyl = *n*-heptyl-*n*-decyl) 4,4'-di-(*p*-*n*-alkoxybenzylideneamino)-2-fluoro-, -chloro-, -bromo-, -iodo-, -methyl-, and -nitro- and -3-chloro-, -bromo-, and -methyl-biphenyls have been recorded. The low mesomorphic thermal stabilities of the 2-substituted derivatives are explained by the steric effects of the angular substituents. An attempt has been made to separate the steric effects of such substituents from their breadth-increasing and polar effects on the mesomorphic thermal stabilities, and to relate the decreases in mesomorphic thermal stability attributed to steric factors alone to calculated values of the interplanar angles, θ , for the 2-substituted biphenyls. The results suggest that the biphenyl nucleus of a *non-sterically* affected system will be more nearly planar in the mesophases than in solution, and may be approximately planar in the smectic mesophase.

LARGE decreases in the mesomorphic thermal stabilities of the 4-*p*-*n*-alkoxybenzylideneaminobiphenyls are brought about by methyl or halogeno-substituents in the 2- or 2'-position of the biphenyl nucleus.¹ These decreases are explained by the increased interplanar angles (θ) for the biphenyl nuclei of the 2- and 2'-substituted derivatives. To find whether other mesomorphic biphenyl derivatives are similarly affected, the 2-substituted 4,4'-di-(*p*-*n*-alkoxybenzylideneamino)biphenyls (I) have now been examined.



The parent compounds ² (I) exhibit smectic and nematic mesophases of high thermal stability, and their 2-substituted derivatives should yield information about the effects of a *range* of substituents on the *smectic* thermal stabilities of sterically hindered biphenyls—with the 4-*p*-*n*-alkoxybenzylideneaminobiphenyls, a 2- or 2'-bromo- or -iodo-substituent destroys the smectic properties.¹ The substituents used in the 2-position of (I) were fluoro-, chloro-, bromo-, iodo-, methyl, and nitro-, and the 3-chloro-, -bromo-, and -methyl-derivatives were made for comparison. The melting points and mesomorphic transition temperatures for these derivatives are listed in Table 1. For each substituent in a given position, four compounds were prepared, R = *n*-heptyl-*n*-decyl. The Table also includes the average decreases [$\Delta t(\text{H-X})$ smectic and nematic] in mesomorphic thermal stability brought about by the substituents.

At this stage it should be noted—see Experimental section—that 3-nitrobenzidine could not be converted into dibenzylidene derivatives. The method employed for the preparation of the dibenzylidene derivatives of the other substituted benzidines gave 4'-*p*-*n*-alkoxybenzylideneamino-4-amino-3-nitrobiphenyls. The melting points of these monobenzylidene derivatives are given in the Experimental section.

The results in Table 1 show that the thermal stabilities of both the smectic and nematic mesophases of (I) are decreased to a greater extent (almost two-fold) by a 2-substituent than by the same 3-substituent. The results therefore support the idea¹ that a 2- or 2'-substituent forces the biphenyl nucleus into a non-planar conformation, so decreasing the intermolecular lateral attractions and the mesomorphic thermal stabilities.

Like the 3-substituted 4-*p*-*n*-alkoxybenzylideneaminobiphenyls, the 3-substituted

¹ Part XI, Byron, Gray, Ibbotson, and Worrall, *J.*, 1963, 2246.

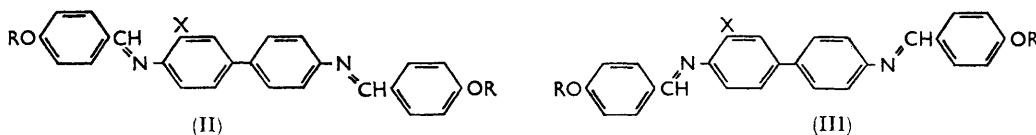
² Gray, Hartley, Ibbotson, and Jones, *J.*, 1955, 4359.

TABLE I.
2- and 3-Substituted 4,4'-di-(*p*-n-alkoxybenzylideneamino)biphenyls.

Substituent	n-Alkyl	Temperature of transition to			Δt (H-X) *	
		Smectic	Nematic	Isotropic	Smectic	Nematic
2-Fluoro-	Heptyl	137°	224·5°	335·5°		
	Octyl	130	240·5	322	58·5° †	29·4°
	Nonyl	124·5	251·5	309		
	Decyl	123	253	296		
2-Chloro-	Heptyl	—	93·5	278·5		
	Octyl	—	117·5	265·5	157·5 †	84·1
	Nonyl	104	129	255		
	Decyl	97	154	244·5		
3-Chloro-	Heptyl	88 ‡	192·5	315		
	Octyl	77 ‡	212·5	302·5	79·5 †	48·4
	Nonyl	80 ‡	225	290		
	Decyl	90 ‡	232	279		
2-Bromo-	Heptyl	—	98·5	262		
	Octyl	—	113	249·5	188 †	99·2
	Nonyl	(90·5) §	103	240		
	Decyl	102·5	123·5	231·5		
3-Bromo-	Heptyl	73·5 ‡	159·5	305·5		
	Octyl	76 ‡	186	293		
	Nonyl	80·5 ‡	203·5	280	97 †	58
	Decyl	86 ‡	214·5	269·5		
2-Iodo-	Heptyl	—	96·5	236		
	Octyl	—	104	228·5	220·5 †	122·6
	Nonyl	(<60)	101·5	216·5		
	Decyl	(91)	102	208·5		
2-Methyl-	Heptyl	—	109·5	277·5		
	Octyl	(111·5) ‡	119·5	264·5	144·5 †	85·4
	Nonyl	106	149	253·5		
	Decyl	95·5	167	243		
3-Methyl-	Heptyl	90 ‡	163	316·5		
	Octyl	99 ‡	187	302·5	96 †	48
	Nonyl	96 ‡	206·5	289·5		
	Decyl	97 ‡	215·5	279·5		
2-Nitro-	Heptyl	(66·5)	107	245·5		
	Octyl	(107·5)	112	235	156 †	104·6
	Nonyl	105	135	225		
	Decyl	105	155·5	216		

* Unless otherwise stated, the average decreases in mesomorphic thermal stability resulting from the introduction of the various substituents are for the four ethers, n-heptyl–n-decyl. † Decreases for the decyl ether only. ‡ Transition temperatures obtained by using a sample contained in a capillary tube, heated by an oil-bath. § Transition temperatures in parenthesis are for monotropic mesophases.

derivatives (I) may adopt two conformations—it is assumed that for reasons of symmetry, the benzylideneamino-groups will adopt a *trans*-arrangement—one (II) in which the benzylideneamino-group and the substituent are *cis*, and the other (III) in which they are *trans* to one another.



The decreases in nematic thermal stability for the 3-substituted dibenzylidene derivatives are smaller than for the 3-substituted monobenzylidene derivatives, but considerably greater than for the 3'-substituted 4'-n-alkoxybiphenyl-4-carboxylic acids [Δt (H-Cl) nematic = 48·4 compared with 31·5°]. The decreases in smectic thermal stability are even larger relative to those for the biphenyl acids [Δt (H-Cl) smectic = 79·5° compared with 30°]. These large decreases may be explained on the basis of either of the conformations. For (II), steric interaction with the 3-substituent will force the benzylideneamino-group out of the plane of the rest of the molecule, whilst for (III), the substituent

protrudes from the exposed 3-position of the rod-shaped parent molecule—both effects would interfere with a parallel packing of the molecules. However, it has been established through studies of a number of substituted mesomorphic compounds, that $\Delta t(X^1-X^2)$ values are fairly constant (provided that $X^1 \neq H$) and may be assigned average values (Table 2) independent of the system, provided that no steric effect operates.

The $\Delta t(Cl-Br)$ values for the 2- and 3-substituted mono- and di-benzylidene derivatives are given in Table 3.

TABLE 2.
Average values of $\Delta t(X^1-X^2)$ smectic and nematic.

	$\Delta t(F-Cl)$	$\Delta t(Cl-Br)$	$\Delta t(Br-I)$	$\Delta t(Me-Cl)$
Smectic	27.75°	11.25°	19.75°	-22.5°
Nematic	24.25	8.25	10.5	2

TABLE 3.
Average values of $\Delta t(Cl-Br)$ for benzylidene derivatives of 4-amino- and 4,4'-diamino-biphenyls.

System	Smectic	Nematic
2-Substituted (dibenzylidene) *	30.5°	15.1°
2-Substituted (monobenzylidene) *	—	18.4
3-Substituted (dibenzylidene)	17.5	9.6
3-Substituted (monobenzylidene)	—	8

* Sterically affected system.

Comparison of the values in Tables 2 and 3 suggests that the 3-substituted derivatives adopt a planar *trans*-arrangement, *i.e.*, (III) above.

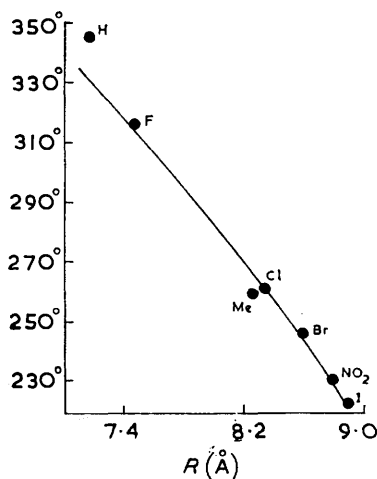


FIG. 1.

Of interest are the changes in the average mesomorphic transition temperatures of the 2-substituted dibenzylidene derivatives with increasing molecular breadth (R) (defined as the diameter of the narrowest cylinder through which the molecule may pass, flexible alkyl chains being assumed not to interfere). Figs. 1 and 3 are the plots of the nematic-isotropic and smectic-nematic transition temperatures, respectively, against R .

Fig. 1 shows that the nematic-isotropic transition temperatures decrease reasonably smoothly with increasing molecular breadth, except that there is a large decrease from $X = H$ to $X = F$. In the case of the non-sterically affected 3'-substituted 4'-*n*-alkoxy-biphenyl-4-carboxylic acids,³ the point for $X = H$ fits the curve for a similar plot of molecular breadth against nematic-isotropic transition temperature. It seems likely that the

³ Gray and Worrall, *J.*, 1959, 1545.

large $\Delta t(\text{H-F})_{\text{nematic}}$ value is explained by a large increase in the interplanar angle, θ , on passing from (I) to the 2-fluoro-derivative. The points for the other substituents must lie on one curve because θ increases proportionately with substituent size, *i.e.*, the $\Delta t(\text{X}^1\text{-X}^2)$ values reflect the combined breadth-increasing and steric effects of the substituents. A similar plot is obtained for the 2-substituted monobenzylidene derivatives¹ (Fig. 2). A larger decrease in nematic-isotropic transition temperature is now observed on passing from $\text{X} = \text{H}$ to $\text{X} = \text{F}$, for as would be expected an increase in θ should have more far reaching effects on the attractions between the smaller molecules of the monobenzylidene derivatives.

In Fig. 2, the open circles are for the smectic-nematic transitions. Only three such temperatures are obtained for the compounds studied, but the large decrease in smectic thermal stability brought about by the relatively small 2-fluoro-substituent is shown.

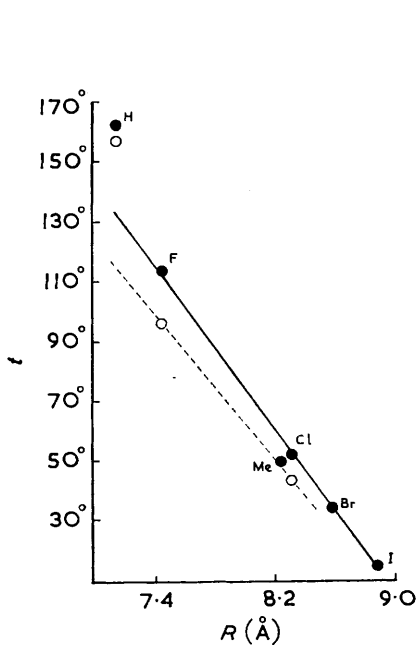


FIG. 2.

● Nematic-isotropic.
○ Smectic-nematic.

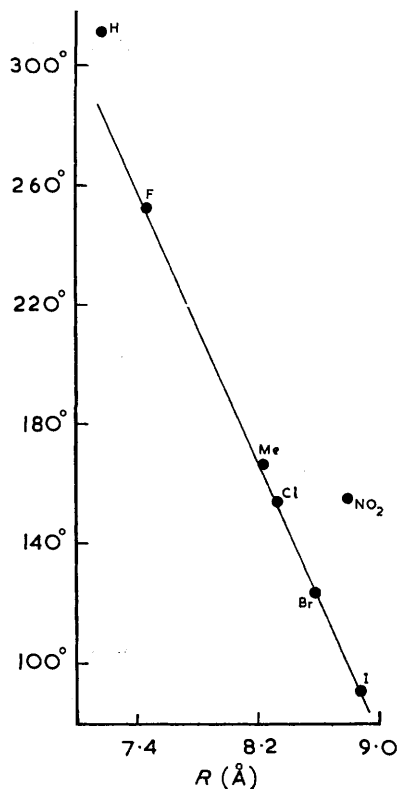


FIG. 3.

Fig. 3 is a plot of the smectic-nematic transition temperatures ($R = n$ -decyl only) for the 2-substituted dibenzylidene derivatives (see Table I) against the molecular breadth (R). The point for $\text{X} = \text{NO}_2$ lies well off the curve through the points for substituents of size greater than fluorine. This is a recognised feature³ of such plots for smectic mesophases, and may be explained by the counteracting influence of the strong ring- NO_2 dipole on the breadth increasing and steric effects of the 2-nitro-group which decrease the smectic thermal stability. Reasoning in this way, the replacement of H by F should have only a small effect on the smectic thermal stability, because the ring-F dipole will enhance the intermolecular attractions. Thus for 3'-fluoro-4'-*n*-octyloxybiphenyl-4-carboxylic acid,³ $\Delta t(\text{H-F})_{\text{smectic}}$ is only 0.5° . The decrease in smectic thermal stability on passing from (I) to its 2-fluoro-derivative is therefore very significant, more so than a simple comparison of Figs. 1 and 3 would suggest.

Dipolar effects of the substituents would not be expected to cause deviations from a smooth curve plot of t against R for the halogeno-derivatives, because the changes in dipole moment on passing from ring-F to ring-I are relatively small. It would, however, have been predicted that the point for $X = \text{Me}$ in Fig. 3 would lie below the curve, because of the low ring-Me dipole. This apparent anomaly will be discussed later.

Both the smectic and nematic mesophases of (I) therefore suffer a large decrease in thermal stability when a 2-fluoro-substituent is introduced. The effect far surpasses the decrease in mesomorphic thermal stability for non-sterically affected systems. We conclude that the interplanar angle θ increases considerably on passing from (I) to the 2-fluoro-derivative. The alternative suggestion that we associate too large a van der Waals radius with hydrogen is unlikely, because the nematic-isotropic transition temperature for 4'-n-octyloxybiphenyl-4-carboxylic acid lies on the curve through the plot of the nematic-isotropic transition temperatures against R for the 3'-substituted derivatives.

If the interplanar angle for the non-sterically affected biphenyl ring system in the mesomorphic states is about the same (45°) as in solution or the gas phase, then no substantial increase in θ would be expected on introducing a 2-fluoro-substituent. The angle θ for the parent mono- and di-benzylidene derivatives must therefore be considerably less than 45° .

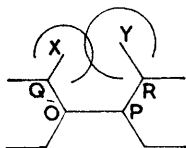


FIG. 4.

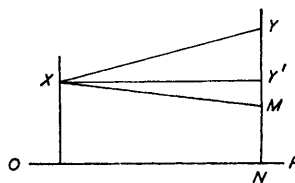


FIG. 5.

To attempt to establish how small θ is in the mesophases of non-sterically affected biphenyl derivatives, it is necessary to know θ for various 2-substituted biphenyls. No X-ray study appears to have been made on the solid states of 2-substituted biphenyls, and it is not easy to obtain values of θ from molecular models. By using co-ordinate geometry, the minimum interplanar angles have therefore been calculated for a range of 2,2'-disubstituted biphenyls, so that the spherical surfaces of the two substituents (X and Y)—see Fig. 4—just touch.

The co-ordinates (origin O) of the centres (X and Y) of the spherical substituents X and Y are:

$$\left. \begin{aligned} X: x_x &= (QX \cos \phi - OQ \cos \phi); y_x = (QX \sin \phi + OQ \sin \phi) \\ Y: x_y &= (OP + PR \cos \phi - RY \cos \phi); y_y = (PR \sin \phi + RY \sin \phi) \end{aligned} \right\} \quad (\text{i})$$

where 2ϕ is the interior angle of the benzene ring.

For no steric interaction, Y must be rotated through an angle (θ) from the OPQ plane to a point Z , such that

$$XZ = (r_x + r_y)$$

where r_x and r_y are the van der Waals radii of X and Y , respectively.

To determine the co-ordinates of the point Z , drop a perpendicular from Y to cut OP in N . Draw XY' parallel to OP to cut YN in Y' , and drop a perpendicular from Z to cut NY in M (Fig. 5).

$$\begin{aligned} NM &= NY \cos \theta \\ MY' &= NY' - NM = y_x - y_y \cos \theta \\ XM^2 &= (MY')^2 + (XY')^2 \\ XZ^2 &= (XM)^2 + (MZ)^2 \end{aligned}$$

$$\text{i.e., } (r_x + r_y)^2 = (y_x - y_y \cos \theta)^2 + (x_y - x_x)^2 + (y_y \sin \theta)^2$$

$$\text{and } \cos \theta = \frac{1}{2y_x y_y} [y_x^2 + y_y^2 + (x_y - x_x)^2 - (r_x + r_y)^2] \quad (\text{ii})$$

By substituting for x_x , x_y , y_x , y_y , r_x , and r_y the values obtained by using the bond lengths and van der Waals radii given in Table 4, values of θ for various 2,2'-disubstituted biphenyls can be calculated. The values of θ so obtained are shown in Table 5.

TABLE 4.
van der Waals radii and bond lengths.

Substituent (X or Y)	van der Waals Radius (r_x, r_y) (Å)	Bond	Length (Å)
H	1.00	C-H	1.07
F	1.35	C-F	1.41
Cl	1.80	C-Cl	1.76
Br	1.95	C-Br	1.91
I	2.15	C-I	2.10
Me	2.00	C-Me	1.54
		(C-C) _{OP}	1.54
		(C-C) _{Oe}	1.39

TABLE 5.
Values of θ for 2,2'-disubstituted biphenyls calculated from equation (ii).

Y \ X	H	F	Cl	Br	I	Me
H	20.1°	41.4°	56.4°	60.1°	64.4°	64.7°
F	41.4	54.8	67.4	69.9	73.6	75.3
Cl	56.4	67.4	77.3	79.9	83.2	85.6
Br	60.1	69.9	79.9	82.4	85.5	87.8
I	64.4	73.6	83.2	85.5	88.5	*
Me	64.7	75.3	85.6	87.8	*	*

* No conformation possible without compression of atomic orbitals.

The angles relevant to the present study are those in column one of Table 5, *i.e.*, when one of the substituents is hydrogen. First it is noted that there is a significant increase in θ on passing from one halogeno-substituent to another, and the increased separation of the molecules resulting from this increase in θ explains why the $\Delta t(\text{Cl-Br})$ values for the 2-substituted mono- and di-benzylidene derivatives are greater than the average value for non-sterically affected systems (*cf.* Tables 2 and 3).

To understand more clearly the dependence of mesomorphic thermal stability on θ , it is necessary to separate the decrease in nematic-isotropic or smectic-nematic transition temperature brought about by a substituent into (a) the decrease due to the breadth-increasing effect of the substituent, and (b) the decrease caused by the steric effect of the substituent. For the 2-substituted derivatives of (I), $\Delta t(\text{H-F})_{\text{nematic}} = 29.4^\circ$, and $\Delta t(\text{H-F})_{\text{smectic}} = 58.5^\circ$. Let x and x' be the decreases in nematic and smectic thermal stability, respectively, brought about solely by the breadth-increasing effect of the fluoro-substituent. Then for the 2-fluoro-substituent, the steric effects on the nematic and smectic thermal stabilities of (I) are given by $\Delta t_s = (29.4 - x)^\circ$ and $(58.5 - x')^\circ$, respectively. Using the decreases in nematic-isotropic transition temperature (average of C_7 - C_{10}) and smectic-nematic transition temperature (C_{10} only) from Table 1, and the $\Delta t(\text{X}^1\text{-X}^2)_{\text{nematic}}$ and smectic values from Table 2, we obtain the following decreases in mesomorphic thermal stability associated with the steric effects of the substituents.

Substituent (X)	F	Cl	Br	I	Me
$\Delta t_s(\text{H-X})_{\text{nematic}}$...	$(29.4 - x)^\circ$	$(59.9 - x)^\circ$	$(66.7 - x)^\circ$	$(79.6 - x)^\circ$	$(63.15 - x)^\circ$
$\Delta t_s(\text{H-X})_{\text{smectic}}$	$(58.5 - x')$	$(129.9 - x')$	$(149 - x')$	$(161.8 - x')$	$(94.3 - x')$

$\Delta t(\text{H-F})$ values vary considerably from one system to another (0.5 – 13° for smectic and 9 – 26.5° for nematic mesophases). The lowest $\Delta t(\text{H-F})_{\text{nematic}}$ and smectic values for the dimeric 3'-substituted 4'-n-alkoxybiphenyl-4-carboxylic acids are used below, because the molecules approximate in size to those of the dibenzylidene derivatives under discussion.

Fig. 6 is the plot of $\Delta t_s(\text{H-X})_{\text{nematic}}$ against θ , $x = 9^\circ$, being used, and Fig. 7 the plot

of $\Delta t_s(\text{H-X})$ smectic against θ , with $x' = 0.5^\circ$, for the 2-substituted 4,4'-di-(*p*-n-alkoxybenzylideneamino)biphenyls.

For the nematic mesophases (Fig. 6), a reasonable curve through the points for the halogeno-substituted compounds can be drawn, and this may comfortably be extrapolated to $\theta = 20.1^\circ$ (the angle calculated for a sterically unaffected biphenyl derivative) with $\Delta t_s(\text{H-X}) = 0^\circ$ (representing zero steric effect relative to hydrogen). The extrapolation requires an increasing gradient of the curve as θ decreases, but it is reasonable to suppose that a given change, $\Delta\theta$, will be less effective in reducing nematic thermal stability at small values of θ than at large values.

The results are therefore consistent with the view that for the nematic mesophase, the angle θ for the non-sterically affected biphenyl ring system of (I) may be about 20° , *i.e.*, much smaller than the angle of 45° for non-sterically hindered biphenyls in solution. If the residual "crystal forces" in the nematic mesophase were able to force the ring system to be more nearly planar, the angle may in fact be less than 20° , but the steepness of the extrapolation to $\theta = 0^\circ$ (broken line in Fig. 6) suggests that the angle cannot be much less than 20° .

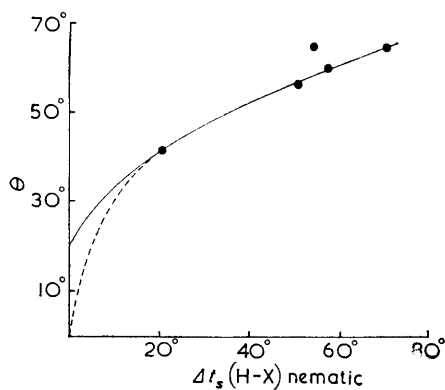


FIG. 6.

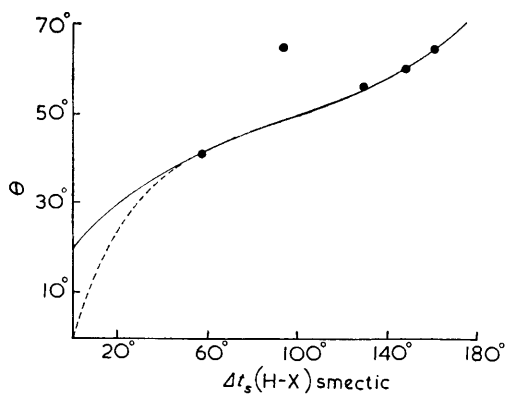


FIG. 7.

From data already published for 2-substituted 4-*p*-n-alkoxybenzylideneaminobiphenyls,¹ a similar treatment for the nematic-isotropic transition temperatures, with $x = 26.5^\circ = \Delta t(\text{H-F})$ nematic for the 3-substituted 4-n-alkoxybenzoic acids, gives a similar result. Extrapolation to $\theta = 20^\circ$ at $\Delta t_s(\text{H-X}) = 0^\circ$ can be readily carried out, suggesting that this is not an unreasonable interplanar angle in the nematic melt.

Fig. 7 represents the trend of $\Delta t_s(\text{H-X})$ smectic with change in θ , and although the curve is quite different in shape from that in Fig. 6, it is noted that the extrapolation to $\Delta t_s(\text{H-X}) = 0^\circ$ at $\theta = 20^\circ$ can be made readily. Indeed the extrapolation could be made to $\theta = <20^\circ$ and even to $\theta = 0^\circ$. Thus the interplanar angle for the non-sterically affected biphenyl ring system may be quite small or even 0° for the smectic state. A lower angle for the smectic mesophase can be reconciled with the fact that the residual "crystal forces" in this mesophase will be greater than for the more disordered nematic melt. In order that $\theta = 0^\circ$ and that the hydrogens in the angular positions are not compressed, the van der Waals radius of hydrogen would have to be 0.88 \AA .

Again, it is clear from these studies that continuous rotation does not occur about the 1,1'-bond of the biphenyl nucleus in the mesomorphic states, and it would appear that the ring system adopts a fixed and as nearly planar arrangement as possible. On this basis it seems legitimate to make comparisons of the mesomorphic thermal stabilities of *different*, non-sterically affected biphenyls, because large differences in θ are unlikely to occur on passing from one system to another.

Two points remain for discussion: (1) The gradient of the curve of $\Delta t_s(\text{H-X})$ smectic

against θ increases from chloro-, to bromo-, to iodo- (Fig. 7), an effect which is absent from the corresponding curve for the nematic mesophases (Fig. 6). The thermal stability of a smectic mesophase depends markedly on the lateral intermolecular attractions contributed to by dipolar and polarisability effects. The polarisability of an aromatic ring should be greatest in the plane of the ring, and least at right angles to the plane. When one of the rings in the biphenyl nucleus is rotated out of the plane, the contribution of the polarisability of this ring to the attractions between the sides of the molecules will decrease slowly at first and then more rapidly as θ increases, *i.e.*, as a function of $\cos \theta$. As θ increases, the polarisability of the ring rotated from the plane will begin to contribute to the interplanar attractions—a function of $\sin \theta$. A combination of these effects would explain the overall shape of the curve in Fig. 7. The less-critical dependence of the thermal stability of the nematic mesophase on the lateral intermolecular attractions, accounts for the absence of a similar upward trend of the curve in Fig. 6 as the size of the 2-substituent becomes larger.

(2) In Figs. 6 and 7, it is clear that the points for methyl do not lie on the curves. This is also found for the 4-*p*-*n*-alkoxybenzylideneamino-2-methylbiphenyls. It suggests that a 2-methyl substituent exerts a smaller steric effect than would be expected for a group of van der Waals radius 2 Å. From Fig. 6, an angle of 58.5°, some 6° less than the calculated angle, would place the point for methyl on the curve, but for the smectic mesophases, an angle as small as 50° is required to bring the point (Fig. 7) near to the line.

The spherical model for the methyl group does not allow for the possible accommodation of the 2'-hydrogen in the interstices of the methyl group, *i.e.*, the H-C-H angle may straddle the 2'-hydrogen, giving a smaller angle than that calculated. In the smectic state, the angle may be further decreased by the stronger residual "crystal forces" exerting stronger forces of compression. Calculations show that to obtain these lower angles, the "effective" van der Waals radii of the methyl group would need to be 1.82 and 1.59 Å for the nematic and smectic mesophases, respectively.

In Fig. 3, the point for X = methyl lies on the curve, whereas it might have been expected to lie below the curve, because of the small Me-ring dipole. The suggestion that the angle θ for the smectic mesophase is considerably smaller than that calculated for a 2-methylbiphenyl, would of course explain the greater smectic thermal stability. In Fig. 1, the point for X = methyl lies slightly below the curve. On the basis of the above arguments it might have been expected to be slightly above the curve. However, the calculated angle θ is *only* some 6° high in the case of the nematic mesophase, which appears to be less sensitive to change in θ than the smectic mesophase. Within the limits of the attempted analysis, the position of the point for methyl in Fig. 1 is therefore reasonably satisfying.

EXPERIMENTAL

Melting points are corrected for exposed stem.

Determination of Transition Temperatures.—Most of the transition temperatures in Table 1 were determined in our usual way by using an electrically heated microscope block⁴ in conjunction with a projection system.⁵ Certain of the solid-smectic transitions were, however, difficult to detect, and where indicated in Table 1, these temperatures were obtained by normal capillary methods.

Materials.—3-Methylazobenzene. This was prepared from *m*-nitrotoluene, aniline, and finely ground sodium hydroxide by Jacobsen's method.⁶ Distillation of the azo-compound [through a Dufton column (15 cm.)] gave 12.7 g. (45.8%), b. p. 170–171°/16 mm. Jacobsen records a b. p. of 175°/19 mm. for 3-methylazobenzene.

2-Methylbenzidine. Zinc dust (5 g.) was added to 3-methylazobenzene (4.9 g., 0.025 mole) in a mixture of ethanol (60 ml.) and acetic acid (10 ml.), and the whole was heated under reflux for 1 hr. The mixture was then filtered hot, allowing the filtrate to run into concentrated

⁴ Gray, *Nature*, 1953, **172**, 1137.

⁵ Gray and Ibbotson, *Nature*, 1955, **176**, 1160.

⁶ Jacobsen, *Ber.*, 1895, **28**, 2541.

hydrochloric acid (70 ml.). The residue of zinc oxide was washed with hot ethanol, the washings being added to the filtrate, and the mixture was heated (15 min.) on a steam-bath, and cooled. The hydrochloride was filtered off and crystallised from 2*N*-aqueous hydrochloric acid, after decolorising with carbon. The crystals (4 g.; 59%) were washed with ethanol saturated with hydrogen chloride, and with ether, and dried under vacuum.

The 2-methylbenzidine dihydrochloride was dissolved in water, and the solution was basified with 2*N*-aqueous ammonia. The free base was extracted with ether and obtained on evaporation as the amorphous glass reported by Jacobsen.⁶ The 4,4'-dibenzylidene derivative (Found: C, 86.4; H, 5.8; N, 7.7. Calc. for C₂₇H₂₂N₂: C, 86.6; H, 5.9; N, 7.5%) (yellow prisms) melted at 112—112.5°, and when the melt was cooled, a nematic mesophase appeared at 88.5° (oil bath). Jacobsen reports m. p. 111—112°, but does not mention the monotropic nematic mesophase.

3-Chloro-, -bromo-, and -methyl-benzidine. An attempt to prepare 3-methylbenzidine from *o*-toluidine, nitrobenzene, and finely ground sodium hydroxide by Jacobsen's method⁶ gave a product which was converted into dibenzylidene derivatives. After purification, the dibenzylidene derivatives² of benzidine were isolated. These derivatives are, in general, less soluble than those of substituted benzidines, and so they accumulate during crystallisation. Crude 2-methylazobenzene obtained from *o*-toluidine and nitrobenzene also gave rise to dibenzylidene derivatives of benzidine, and this has been observed for other azo-compounds prepared by this method. A source of the benzidine precursor could be nitrosobenzene which may give azoxybenzene, as demonstrated by Ingold⁷ for *p*-bromonitrosobenzene which, merely by steam-distillation, gave *p*-bromonitrobenzene and 4,4'-dibromoazoxybenzene. In view of these comments, it seems highly fortuitous that 3-methylazobenzene is obtained apparently pure by Jacobsen's method.

Pure 2-chloro-, -bromo-, and -methyl-azobenzene were obtained from the *o*-substituted anilines and nitrosobenzene by chromatographing the products on alumina. These preparations and the conversions into the benzidines are described below, although when this work was completed, Belcher, Nutten, and Stephen⁸ independently published methods for obtaining the 2-chloro- and -bromo-azobenzenes pure by chromatography. Their yields were some 10—15% lower than by the present methods.

2-Chloroazobenzene. Nitrosobenzene (12 g., 1 mol.) and *o*-chloroaniline (17.9 g., 1.25 mol.) were dissolved separately in acetic acid (35 ml.), and the solutions mixed. The olive-green solution was kept for 48 hr. at room temperature. The now orange-red mixture was added to water (2 l.), the oil extracted with ether, and the extract washed with water, 2*N*-aqueous hydrochloric acid, and water. Removal of the ether and prolonged steam-distillation of the residue gave the crude product. A dry solution of the azo-compound in benzene (40 ml.) was adsorbed on alumina (26 × 4.9 cm.). Equal volume fractions of eluate (benzene, 30 ml.) were collected, and the 2-chloroazobenzene (14.2 g., 58.5%), m. p. 31—33°, was obtained from fractions 2—5 inclusive. Belcher *et al.*⁸ report m. p. 33°.

2-Bromoazobenzene. This was obtained in an identical manner from *o*-bromoaniline (24.1 g.). The yield was 12.1 g. (41.5%), m. p. 34—36°. Belcher *et al.*⁸ record a m. p. of 36°.

2-Methylazobenzene. Using *o*-toluidine (15 g.), the procedure for the 2-chloro-derivative was followed, the temperature of the reactants being kept below 30°, and the mixture being left for only 24 hr. Nine fractions (30 ml.) of benzene eluate were collected. From samples of the products from these fractions, it was established by reduction, rearrangement of the hydrazo-compound, and conversion into the 4,4'-dibenzylidene-derivative, that the last four fractions gave 4,4'-dibenzylidenebenzidine, m. p. 232°. The dianil from fraction 6 had m. p. 136°, only 2° higher than the m. p. reported by Jacobsen⁶ for 4,4'-dibenzylideneamino-3-methylbiphenyl. The red oils from fractions 2—5 inclusive were therefore taken to be 2-methylazobenzene (6 g., 27.4%).

3-Chloro-, -bromo-, and -methyl-benzidine. These were obtained from the azo-compounds as described for 2-methylbenzidine. 3-Chlorobenzidine (yield of dihydrochloride, 59%) was crystallised from aqueous ethanol and from light petroleum (b. p. 40—60°). The colourless needles had m. p. 75.5—76.5°. Belcher *et al.*⁸ record m. p. 75°. The *diacetyl* derivative had m. p. 287—287.5° (Found: C, 63.3; H, 4.8; Cl, 11.3; N, 9.2. C₁₆H₁₅ClN₂O₂ requires C, 63.5; H, 5.0; Cl, 11.7; N, 9.3%), and the 4,4'-dibenzylidene-derivative (Found: C, 79.4; H, 5.0;

⁷ Ingold, *J.*, 1925, 516.

⁸ Belcher, Nutten, and Stephen, *J.*, 1958, 2338.

Cl, 8.7; N, 7.1. $C_{26}H_{19}ClN_2$ requires C, 79.1; H, 4.8; Cl, 9.0; N, 7.1%) was obtained as yellow needles, m. p. 147°, the nematic-isotropic transition temperature being 188.5° (oil-bath).

3-Bromobenzidine (yield of dihydrochloride, 56%) was crystallised as for the 3-chloro-derivative; the needles had m. p. 80—81° (Belcher *et al.*⁸ report the same m. p.). The *diacetyl* derivative (Found: C, 55.4; H, 4.5; Br, 22.8; N, 7.9. $C_{16}H_{15}BrN_2O_2$ requires C, 55.5; H, 4.3; Br, 23.1; N, 8.1%) had m. p. 273—275°, and the 4,4'-*dibenzylidene* derivative (Found: C, 71.3; H, 4.5; Br, 17.8; N, 6.4. $C_{26}H_{19}BrN_2$ requires C, 71.1; H, 4.3; Br, 18.2; N, 6.4%), m. p. 137°, gave a nematic-isotropic transition at 178° (oil-bath).

3-Methylbenzidine (yield of dihydrochloride, 53%) was a glass and was characterised by preparing the 4,4'-*dibenzylidene* derivative (Found: C, 86.4; H, 5.9; N, 7.3. Calc. for $C_{22}H_{22}N_2$: C, 86.6; H, 5.9; N, 7.5%) which melted at 137° and gave a nematic-isotropic transition at 180.5° (oil-bath). Jacobsen⁶ obtained m. p. 134°, but did not mention the mesophase.

3-Fluoroazobenzene. This was prepared as described for 2-chloroazobenzene and purified by chromatography on alumina. The single red band was eluted in benzene (25 ml.). Evaporation gave 3-fluoroazobenzene (2 g., 21%), m. p. 42—45° (Found: C, 72.2; H, 4.9; N, 14.2. $C_{12}H_9FN_2$ requires C, 72.0; H, 4.5; N, 14.0%).

2-Fluorobenzidine was prepared by the method for 2-methylbenzidine, and crystallised twice from benzene-light petroleum (b. p. 40—60°). The pale brown needles of the *fluoro-amine* (1.7 g., 42%), m. p. 103.5—104.5° (Found: C, 71.4; H, 5.6; N, 13.7. $C_{12}H_{11}FN_2$ requires C, 71.3; H, 5.5; N, 13.9%).

It was not possible to obtain pure samples of 2-chloro- and 2-bromo-benzidine by the method used for 2-fluorobenzidine or by reduction of the appropriate dinitro-compounds. The products gave impure dibenzylidene derivatives. 2-Iodobenzidine was successfully obtained from *NN'*-diacetyl-2-aminobenzidine by the method of Schin-ichi Sako.⁹ This method gave pure 2-chloro- and 2-bromo-benzidine, although the final deacetylations were troublesome. The only satisfactory procedure involved ethanolic hydrochloric acid or hydrobromic acid, although the yields were not good.

2-Nitrobenzidine. This (95—98%), m. p. 143°, was prepared by Tauber's method.¹⁰

NN'-Diacetyl-2-aminobenzidine. 2-Nitrobenzidine was acetylated, and the product reduced in 62.5% yield to *NN'*-diacetyl-2-aminobenzidine, m. p. 260—261°, as described by Schin-ichi Sako,⁹ who recorded m. p. 260—262°. The amine can be obtained as very pale yellow needles, m. p. 263—263.5°, from nitrobenzene.

NN'-Diacetyl-2-chlorobenzidine. Ice-cold 15% hydrochloric acid (48 ml.) and powdered *NN'*-diacetyl-2-aminobenzidine (8 g., 0.0283 mole) were thoroughly mixed. Cold water (21 ml.) was added and the paste diazotised by adding powdered sodium nitrite (2.2 g., 0.319 mole) at -3°. 45 Min. after the addition, the excess of nitrous acid was destroyed (sulphamic acid). The suspension of red diazonium chloride was added to ice-cold cuprous chloride (2.8 g., 0.0283 mole) in 15% hydrochloric acid. Decomposition was complete after 48 hr. at room temperature. The yellow solid was filtered off and washed well with 2*N*-aqueous hydrochloric acid, water, and ethanol. Two crystallisations from nitrobenzene gave *NN'*-diacetyl-2-chlorobenzidine (4 g., 46.7%), m. p. 308—309°. Further crystallisations raised the m. p. to 310° (Found: C, 63.8; H, 5.0; Cl, 11.8; N, 8.9. $C_{16}H_{15}ClN_2O_2$ requires C, 63.5; H, 5.0; Cl, 11.7; N, 9.3%).

2-Chlorobenzidine. The diacetyl derivative (2.7 g.) was heated under reflux at 100° in an oil-bath (2 hr.) using a mixture of ethanol (36 ml.) and concentrated hydrochloric acid (9 ml.). The mixture was cooled and the dihydrochloride (2 g.) was filtered off and dissolved in water (75 ml.), and the solution basified with 2*N*-aqueous ammonia. The brown emulsion was extracted with carbon tetrachloride, leaving an insoluble gum. On evaporation, the dried extract gave the diamine, m. p. 98—101°. The 2-chlorobenzidine crystallised from benzene-light petroleum (b. p. 40—60°) as pale orange needles (0.8 g., 41.3%), m. p. 102° (Found: C, 65.7; H, 5.0; Cl, 16.3; N, 12.7. $C_{12}H_{11}ClN_2$ requires C, 65.9; H, 5.0; Cl, 16.3; N, 12.8%). Burns, McCombie, and Scarborough¹¹ have reported m. p. 113° for 2-chlorobenzidine.

NN'-Diacetyl-2-bromobenzidine. This was prepared as described for the 2-chloro-compound, by using 7% hydrobromic acid (120 ml.) and water (53 ml.) for 20 g. of the amine. Cuprous bromide (8.15 g., 1 mol.) dissolved in 7% hydrobromic acid (120 ml.) was used to form the

⁹ Schin-ichi Sako, *Bull. Chem. Soc. Japan*, 1934, 9, 150.

¹⁰ Tauber, *Ber.*, 1890, 23, 796.

¹¹ Burns, McCombie, and Scarborough, *J.*, 1928, 2935.

complex which was decomposed during about 30 min. at 45–50°. The crude product (22.5 g.) was filtered off, washed with 2N-aqueous hydrobromic acid, water, and ethanol, and crystallised twice from nitrobenzene. The *bromo-compound* (12.5 g., 51%) was obtained as pale orange needles, m. p. 312–313°. Further crystallisations raised the m. p. to 314° (Found: C, 55.5; H, 4.5; Br, 23.4; N, 8.2. $C_{16}H_{15}BrN_2O_2$ requires C, 55.3; H, 4.3; Br, 23.1; N, 8.1%).

2-Bromobenzidine. The diacetyl derivative (16 g.) was hydrolysed by using ethanol (80 ml.) and 60% hydrobromic acid (23 ml.), as described for the chloro-analogue. Evaporation of the carbon tetrachloride extract gave *2-bromobenzidine*, m. p. 98–100°, which was crystallised from benzene–light petroleum (b. p. 40–60°) yielding needles (2 g., 44%), m. p. 101° (Found: C, 54.5; H, 4.3; Br, 30.6; N, 10.6. $C_{12}H_{11}BrN_2$ requires C, 54.8; H, 4.2; Br, 30.4; N, 10.6%).

2-Iodobenzidine. The diacetyl derivative was prepared (17%) from *NN'*-diacetyl-2-aminobenzidine and hydrolysed with ethanolic sulphuric acid, following the method of Schin-ichi Sako.⁹ The product was a brown gum (85%) which would not crystallise, but was satisfactory for preparing the dibenzylidene derivatives, for which analyses are tabulated below.

TABLE 6.

4'-*p*-Alkoxybenzylideneamino-4-amino-3-nitrophenyls.

Alkyl	Found (%)			Formula	Required (%)		
	C	H	N		C	H	N
<i>Heptyl</i>	72.4	6.7	9.5	$C_{36}H_{29}N_3O_3$	72.4	6.7	9.7
<i>Octyl</i>	72.7	7.0	9.4	$C_{37}H_{31}N_3O_3$	72.8	6.95	9.4
<i>Nonyl</i>	73.3	7.1	9.3	$C_{38}H_{33}N_3O_3$	73.2	7.2	9.15
<i>Decyl</i>	73.6	7.3	8.8	$C_{39}H_{35}N_3O_3$	73.6	7.4	8.9

TABLE 7.

2- and 3-Substituted 4,4'-di-(*p*-n-alkoxybenzylideneamino)biphenyls.

Subst.	Alkyl	Found (%)				Formula	Required (%)			
		C	H	Hal	N		C	H	Hal	N
2-Fluoro-	<i>Heptyl</i>	79.5	7.8		4.6	$C_{40}H_{47}FN_2O_2$	79.2	7.8		4.6
	<i>Octyl</i>	79.6	8.3		4.4	$C_{42}H_{51}FN_2O_2$	79.5	8.0		4.4
	<i>Nonyl</i>	79.7	8.4		4.2	$C_{44}H_{55}FN_2O_2$	79.8	8.3		4.2
2-Chloro-	<i>Decyl</i>	80.2	8.7		4.3	$C_{46}H_{59}FN_2O_2$	80.0	8.6		4.1
	<i>Heptyl</i>	77.1	7.7	5.5	4.3	$C_{40}H_{47}ClN_2O_2$	77.1	7.6	5.7	4.5
	<i>Octyl</i>	77.6	8.0	5.5	4.1	$C_{42}H_{51}ClN_2O_2$	77.5	7.8	5.5	4.3
3-Chloro-	<i>Nonyl</i>	77.9	8.2	5.1	4.2	$C_{44}H_{55}ClN_2O_2$	77.8	8.1	5.2	4.1
	<i>Decyl</i>	77.9	8.4	5.2	4.1	$C_{46}H_{59}ClN_2O_2$	78.1	8.3	5.0	4.0
	<i>Heptyl</i>	76.9	7.8	5.5	4.7					
2-Bromo-	<i>Octyl</i>	77.7	7.8	5.4	4.3					
	<i>Nonyl</i>	77.9	8.1	5.1	4.3					
	<i>Decyl</i>	78.2	8.2	5.2	4.2					
3-Bromo-	<i>Heptyl</i>	71.8	6.9	12.2	4.5	$C_{40}H_{47}BrN_2O_2$	72.0	7.1	12.0	4.2
	<i>Octyl</i>	72.6	7.4	11.7	4.0	$C_{42}H_{51}BrN_2O_2$	72.5	7.3	11.5	4.0
	<i>Nonyl</i>	73.1	7.7	11.4	4.1	$C_{44}H_{55}BrN_2O_2$	73.0	7.6	11.1	3.9
2-Iodo-	<i>Decyl</i>	73.6	7.8	10.9	3.6	$C_{46}H_{59}BrN_2O_2$	73.5	7.9	10.7	3.7
	<i>Heptyl</i>	72.0	6.9	12.2	4.2					
	<i>Octyl</i>	72.8	7.2	11.5	4.1					
3-Iodo-	<i>Nonyl</i>	73.2	7.5	10.8	3.9					
	<i>Decyl</i>	73.2	7.9	10.6	3.5					
	<i>Heptyl</i>	67.4	6.7	17.5	3.9	$C_{40}H_{47}IN_2O_2$	67.2	6.6	17.9	3.9
2-Methyl-	<i>Octyl</i>	68.0	6.8	16.6	3.5	$C_{42}H_{51}IN_2O_2$	67.9	6.9	17.1	3.8
	<i>Nonyl</i>	69.0	6.9	16.0	3.6	$C_{44}H_{55}IN_2O_2$	68.6	7.1	16.5	3.6
	<i>Decyl</i>	68.9	7.6	16.3	3.7	$C_{46}H_{59}IN_2O_2$	69.2	7.4	15.9	3.5
3-Methyl-	<i>Heptyl</i>	81.6	8.1		4.6	$C_{41}H_{50}N_2O_2$	81.7	8.3		4.65
	<i>Octyl</i>	81.8	8.7		4.4	$C_{43}H_{54}N_2O_2$	81.9	8.6		4.45
	<i>Nonyl</i>	82.3	8.9		4.2	$C_{45}H_{58}N_2O_2$	82.1	8.8		4.25
2-Nitro-	<i>Decyl</i>	82.4	8.8		4.2	$C_{47}H_{62}N_2O_2$	82.2	9.0		4.1
	<i>Heptyl</i>	81.8	8.3		4.4					
	<i>Octyl</i>	82.0	8.7		4.3					
3-Nitro-	<i>Nonyl</i>	81.9	8.9		4.2					
	<i>Decyl</i>	82.4	9.0		4.0					
	<i>Heptyl</i>	75.6	7.5		6.7	$C_{40}H_{47}N_3O_4$	75.8	7.5		6.6
2-Nitro-	<i>Octyl</i>	76.3	7.6		6.4	$C_{42}H_{51}N_3O_4$	76.2	7.8		6.35
	<i>Nonyl</i>	76.6	8.2		6.0	$C_{44}H_{55}N_3O_4$	76.6	8.0		6.1
	<i>Decyl</i>	77.1	8.4		5.8	$C_{46}H_{59}N_3O_4$	77.0	8.3		5.85

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3-Nitrobenzidine. 4-Amino-3,4'-dinitrobiphenyl¹² was selectively reduced as described by Case,¹³ who did not purify the product. The crude material was crystallised from ethanol-chlorobenzene (2 : 1 by volume). The fine, dark brown needles of 3-nitrobenzidine (42%) had m. p. 210—211°, agreeing with the m. p. (208—210°) recorded by Le Fèvre and Turner.¹²

Preparation of Di-p-n-alkoxybenzylidene Derivatives.—To the diamine (0.15—0.30 g., 1 mol.) in hot ethanol (25 ml.), the *p*-n-alkoxybenzaldehyde (2.2 mol.) and a few drops of acetic acid were added, and, in general, the reaction was complete after heating for some 15 min. on a boiling-water bath. The product was allowed to crystallise from the solution and was recrystallised from ethanol or ethanol-benzene, and from benzene or benzene-light petroleum (b. p. 40—60°), until the m. p. and mesomorphic transition temperatures were constant.

When this method was applied to 3-substituted benzidines, there were two complicating features, (a) the lower reactivity of the sterically blocked 4-amino-group relative to the 4'-amino-group, and (b) the insolubility of the initially formed 4'-benzylidene derivative which precipitates from solution. The addition of benzene to the mixture overcomes the solubility difficulty, but inhibits the further reaction of the mono-derivative. The benzylidene derivatives of 3-chloro- and 3-bromo-benzidine were prepared as follows:

The *p*-n-alkoxybenzaldehyde (3 mol.) was added to the diamine (0.3 g., 1 mol.) in hot acetic acid (15 ml.), and the mixture was heated for 30 min. on the water bath. Any solid which separated was then filtered off and rejected. The crystalline product was collected from the cooled filtrate and recrystallised to constant m. p. as described in the first method.

With 3-nitrobenzidine, only 4'-*p*-n-alkoxybenzylideneamino-4-amino-3-nitrobiphenyls could be obtained. The products were not mesomorphic, and by using the microscope heating block⁴ and the projection system,⁵ the following m. p.s were obtained: n-heptyl, 188.5°; n-octyl, 186°; n-nonyl, 184.5°; n-decyl, 182.5°.

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¹² Le Fèvre and Turner, *J.*, 1928., 253.

¹³ Case, *J. Amer. Chem. Soc.*, 1938, **60**, 424.
